

CHEMICAL ANALYSIS BY INFRARED

by BRYCE CRAWFORD, JR.

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Chemical Analysis by Infrared

*Electromagnetic waves make the atoms in a compound vibrate.
The frequencies to which a substance responds can tell much
about its structure and about the nature of chemical bonds*

by Bryce Crawford, Jr.

Infrared spectroscopy has grown like a mushroom in the past 10 years. Before the war it was employed by only a few chemists and physicists, using home-built or custom-built infrared spectrometers. Now the instrument is a standard commercial item supplied by a competitive industry to chemical and medical researchers all over the country.

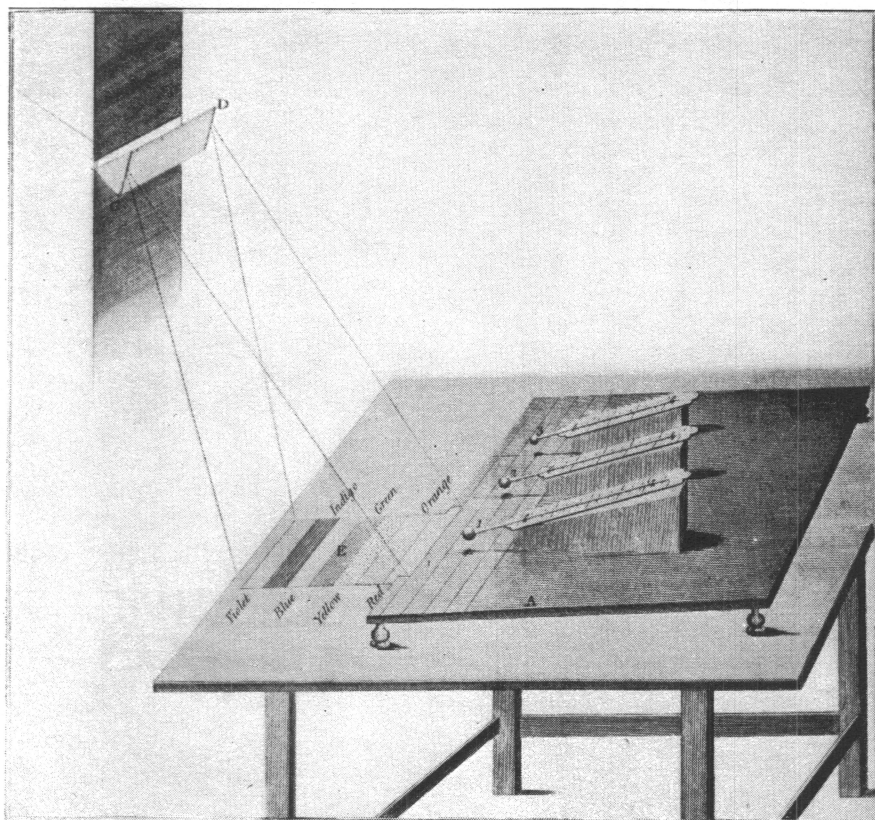
More than 1,300 commercial infrared spectrometers, each representing an investment of two to six Cadillacs, are earning their way in scientific laboratories and industrial plants.

To an old-timer in the field—"old-timer" by virtue of having studied infrared as long as, say, 15 years—this burgeoning use of infrared by his col-

leagues is most gratifying, but hardly surprising. The power of infrared as a tool for chemical characterization and analysis has been known for some 20 years. The infrared spectrum of a substance is related to its chemical structure in a uniquely convenient way, and organic chemists have been heard to say that the infrared spectrum of an organic compound is its most important physical property.

Infrared radiation itself was discovered more than 150 years ago, long before scientists had any clear understanding of radiation. Sir William Herschel, who started life as an organist at Bath and became an astronomer, made the discovery. In 1800 he reported to the Royal Society certain experiments in heat radiation. He resolved sunlight into its spectrum with a glass prism and placed a thermometer at successive positions in the spectrum. He found heat radiation not only in the visible spectrum but in the longer wavelengths beyond the red. Herschel even crudely measured the absorption of this radiation by various substances, including tap water, distilled water, sea water, gin and brandy. He could not know, could not even suspect, how revealing the absorption could be about chemical structure. Before anyone could appreciate the significance of infrared absorption, light radiation itself had to be understood. A century passed before the theory of the nature of light was worked out and the necessary techniques and instruments for infrared analysis were developed.

Sir William had found that the most intense heat radiations were outside the visible part of the spectrum. Conse-



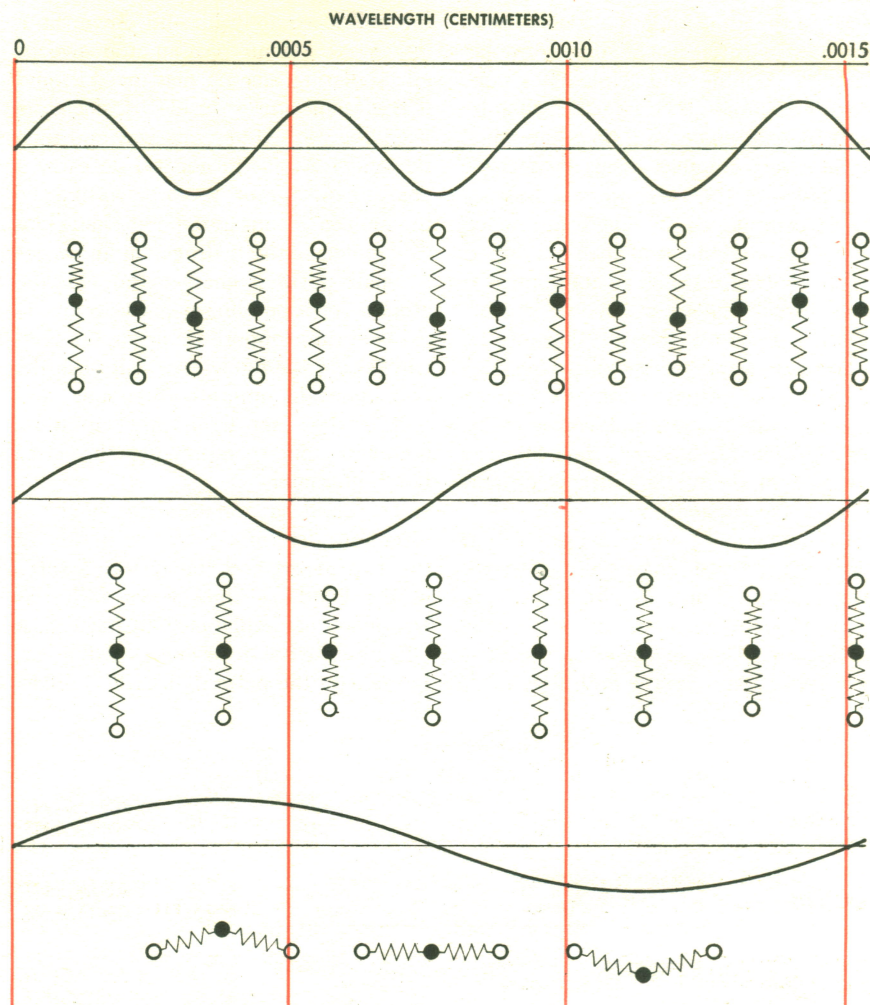
FIRST INFRARED SPECTROMETER, improvised by Sir William Herschel in 1800, was the means by which he discovered infrared radiation. Thermometers placed in successive bands of solar spectrum registered more heat outside and beyond red region than within.

quently for many years it was believed that heat and light were two quite different radiations. But some 35 years later Sir William's son, Sir John Herschel, and other investigators advanced the idea that heat and light might merely be different manifestations of the same radiation—that is, light waves of different wavelengths. Before the end of the century James Clerk Maxwell had shown theoretically and Heinrich Hertz had proved experimentally the essential identity of light, heat and other electromagnetic radiation.

The infrared region, as spectroscopists usually define it, lies between the visible and the radio portions of the spectrum—that is, the wavelengths between one thousandth of a millimeter and one millimeter. (Infrared of course is not synonymous with the common meaning of the word "heat," for, as we have seen, there are heat radiations in the visible part of the spectrum.) The region most useful to the chemist is the range of wavelengths from 2 to 20 microns (thousandths of a millimeter). This is sometimes called the vibrational region.

We shall confine ourselves to this region and to considering how absorption spectra in it give information about matter. The other infrared regions, and the physics of the radiation itself, are just as interesting: it was in the near infrared that Max Planck, by instinct and gentle nature one of the most classical of physicists, was led to the disturbing idea of the quantum, which upset the whole beautiful pattern of 19th-century physics. But we cannot cover the whole subject of infrared in one article.

The chemically useful study of infrared absorption spectra was really begun in 1903 at Cornell University. A graduate student named William W. Coblentz, under the physics professor Edward Nichols, had undertaken research on infrared absorption. After improving the available experimental techniques, he received an appointment as a research associate of the Carnegie Institution of Washington, which enabled him to set about measuring absorption spectra of pure substances. He mapped spectra for two years and in 1905 published a collection of accurate infrared absorption spectra for 131 substances. Even today, after 48 years of improvements in infrared technique (to which Coblentz himself contributed much until his retirement from the National Bureau of Standards in 1945) the monumental work that he did at Cornell still stands worthy of study. Subsequent studies



VIBRATION OF MOLECULAR BONDS accounts for selective absorption of infrared energy by various compounds. Each of three modes of vibration of carbon dioxide bonds shown here is resonant to infrared at wavelength indicated. Energy is absorbed, however, only by modes at top and bottom, which disturb geometric and electric symmetry of atom.

have confirmed more than they have corrected Coblentz's observations.

When sunlight falls upon a green leaf of a tree, the leaf absorbs the red wavelengths of the light and reflects the green wavelengths: this is what gives the leaf its color. The absorption tells something about the leaf's molecular composition. Essentially the same principle is involved in studying infrared absorption, except that the radiation is not visible; if our eyes were attuned to the infrared, we could recognize a compound by its characteristic color. Instead we measure its absorption of heat. Infrared radiation is passed through a solution of a compound, and the compound characterizes itself by the wavelengths it absorbs and those it transmits. Each compound has its own absorption spectrum.

The absorption of infrared is due to some disturbance within the molecule; this Coblentz established by observing that he got different spectra from isomers—molecules which are composed of

the same atoms but in different arrangements. Coblentz found further that certain subgroupings of atoms within molecules identified themselves by absorbing characteristic wavelengths: for example, phenyl compounds, containing the benzene ring, absorbed at 3.25 and 6.75 microns, while mustard oils, containing the thiocyanate group, absorbed at 4.78 microns. These absorptions were additive: in phenyl mustard oil Coblentz found "the characteristic vibration of the mustard oils superposed upon the vibration of the benzene nucleus." He concluded that "there is a something—call it 'particle,' 'group of atoms,' 'ion' or 'nucleus'—in common, with many of the compounds studied, which causes absorption bands that are characteristic of the great groups of organic compounds, but we do not know what that 'something' is."

With half a century's progress since Coblentz, we now have a clear idea of the "something." It lies in the bonds

between the atoms in a molecule. These bonds are written in chemical formulas as single, double and triple lines connecting the atoms. As the Danish chemist Niels Bjerrum once said, they "summarize, in a very compact form, chemistry's knowledge of the creation and destruction of compounds. Nowhere in science has a shorthand notation been developed which summarizes such an abundance of exact knowledge in so small a space." In 1914 Bjerrum showed that, if we think of the atoms as small masses and the bonds as springs holding the atoms together, we can account correctly for the vibrational behavior of molecules, as observed in their infrared spectra and in their heat capacities.

The bonds hold the atoms in position fairly tightly, but not rigidly. The response of the atoms to a light wave is much like the response of cork balls, floating on a lake, to waves on the lake. As waves move past the ball, they push

the ball alternately up and down. So a light wave moving past an atom sweeps an oscillating electric field over it, and if the atom carries an electrical charge it will be pushed first one way and then the other. Atoms in general do carry a charge, greater or lesser according to the molecule; thus in the hydrogen chloride molecule the hydrogen atom carries a small positive charge, the chlorine atom a corresponding negative one. Because of these opposite charges, the electric field of the light wave will push the two atoms in opposite directions, and will tend to set them into vibration, stretching and compressing the H-Cl bond alternately.

The bond has a natural frequency of vibration, determined by the masses of the two atoms and the restoring force of the bonds. A light wave with this frequency of oscillation will have most effect on the bond: its energy will greatly increase the natural vibrations of the

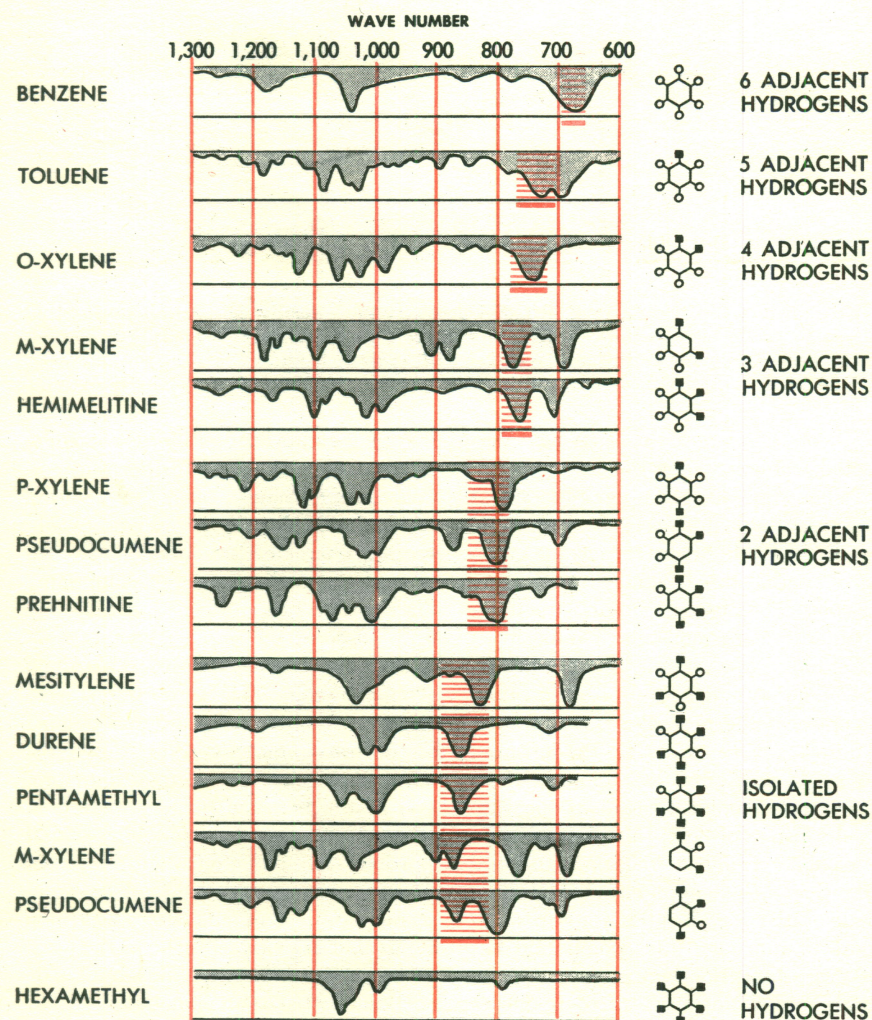
atoms. The molecule will absorb part of the energy of the light at this resonant frequency, and an absorption detector will show an absorption peak for that wavelength.

To obtain the infrared spectrum of a sample, we illuminate the sample with infrared radiation of successive wavelengths from 2.5 to 25 microns and measure with the spectrometer the amount of light transmitted by the sample at each wavelength. A modern spectrometer automatically computes the percentage of the light transmitted at each wavelength and in 10 or 15 minutes produces a curve of transmittance against wavelength, or, more commonly nowadays, transmittance against frequency. Frequency, meaning the number of waves that sweep past per second, is easily computed from the wavelength and the speed of light. The measure of frequency is called the "wave number"—it is actually the number of waves in one centimeter of light beam. In the range of infrared that we are considering the wave numbers run from 400 to 4,000 per centimeter.

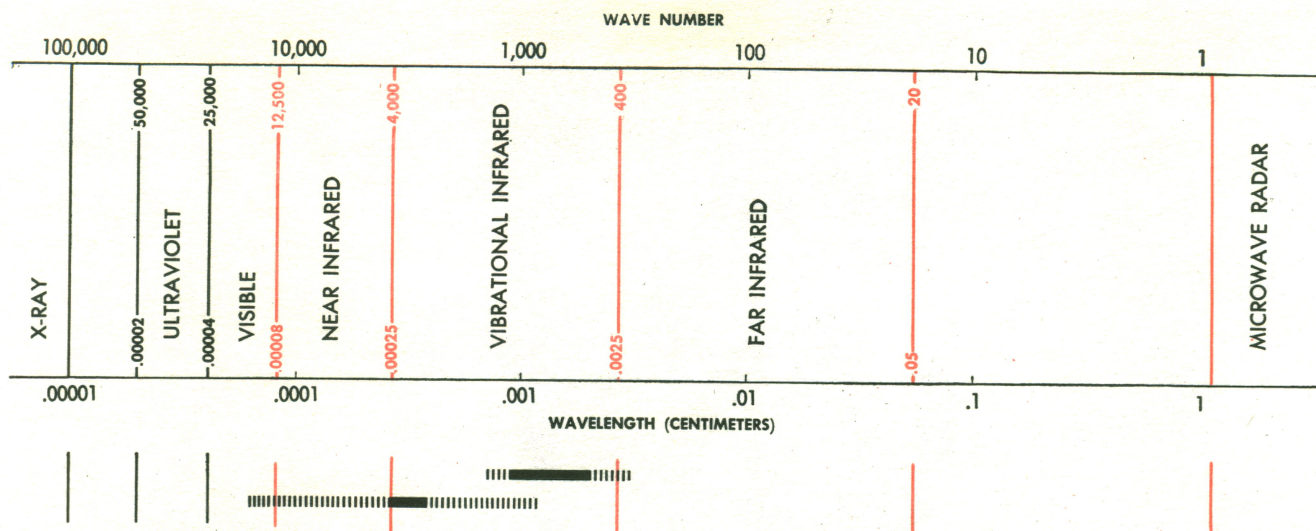
Modern atomic theory at once shows the chemical importance of the frequency of absorption. Atoms and molecules absorb light in quanta, the energy in each quantum being proportional to the frequency of the light. The absorbed energy is in fact Planck's constant h times the frequency, or hc times the wave number. Einstein enunciated the principle that, when molecules absorb light, each quantum is wholly absorbed by one molecule.

Now a molecule can safely absorb only so much energy: chemical bonds are not unbreakable—and a good thing, or there'd be no chemistry! The energy required to break the bonds is known fairly accurately; it is comparable to the energy of a quantum of ultraviolet or visible light. When a molecule absorbs such light, the bonds are either broken or profoundly altered, and the "excited" molecule is a very different entity from the original. The deduction of atomic structure from ultraviolet spectra has been compared to deducing the structure of a piano from the sounds emitted as it falls down a flight of stairs.

The absorption of a quantum in the infrared, on the other hand, is not so rough a process. At these wavelengths a quantum of energy is only about one twentieth that in the ultraviolet. Hence the radiation merely sets the bond into vibration. In infrared spectroscopy we don't push the piano down the stairs,

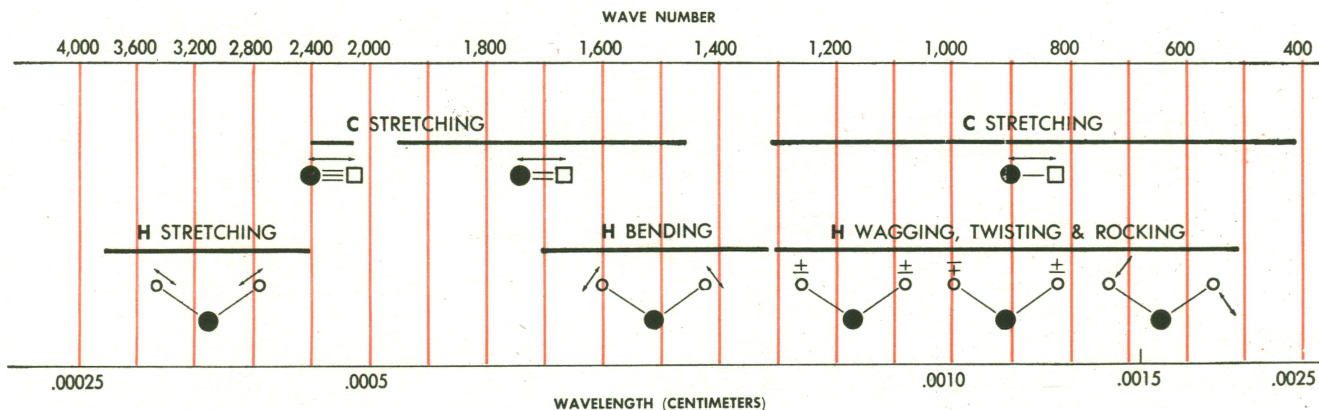


RELATED FAMILY of compounds, the methyl benzenes, exhibit both an over-all similarity and distinctive differences in their infrared spectra. The absorption dips which are marked in red are due to hydrogen wagging (see middle diagram on the facing page). The hydrogen atoms are vibrating in and out of, in a direction perpendicular to, the page surface.



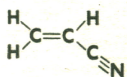
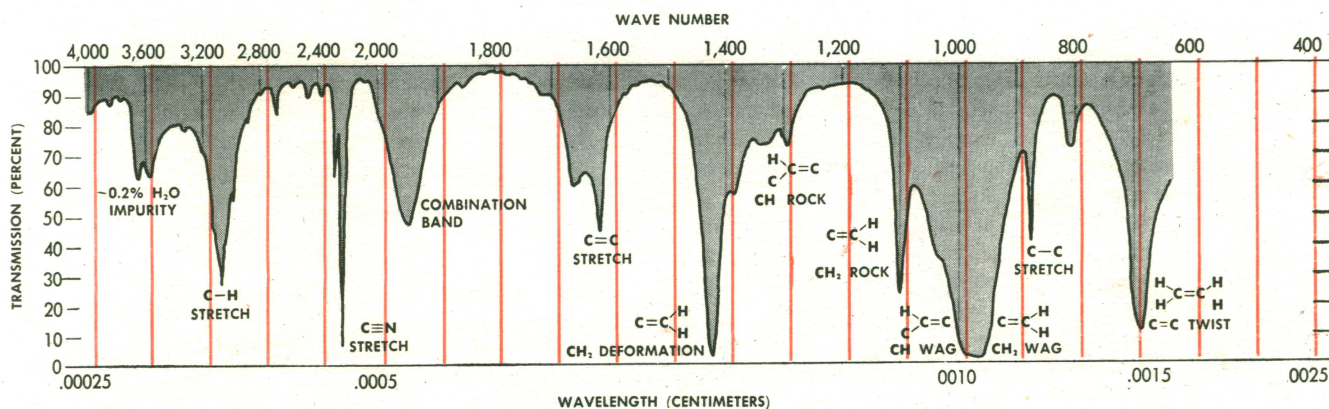
ELECTROMAGNETIC SPECTRUM is diagrammed above. Wave number means the number of wavelengths per centimeter and is proportional to frequency. Wave numbers from 400 to 4,000 have the right frequency to excite molecular vibrations. Bars below

locate concentrations of heat radiation from a black body at 80 degrees F. (*upper bar*) and 1,800 degrees (*lower*). In each bar 50 per cent of the total heat energy is in the black sections, 40 per cent in the broken section, and the rest tapers off from the ends.



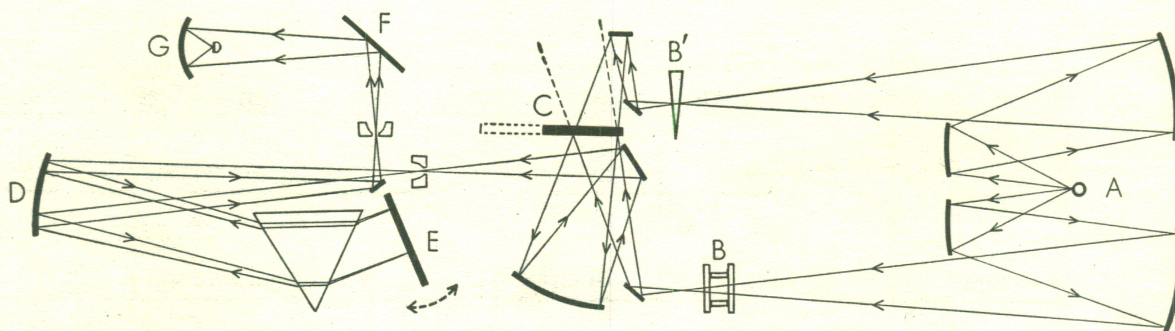
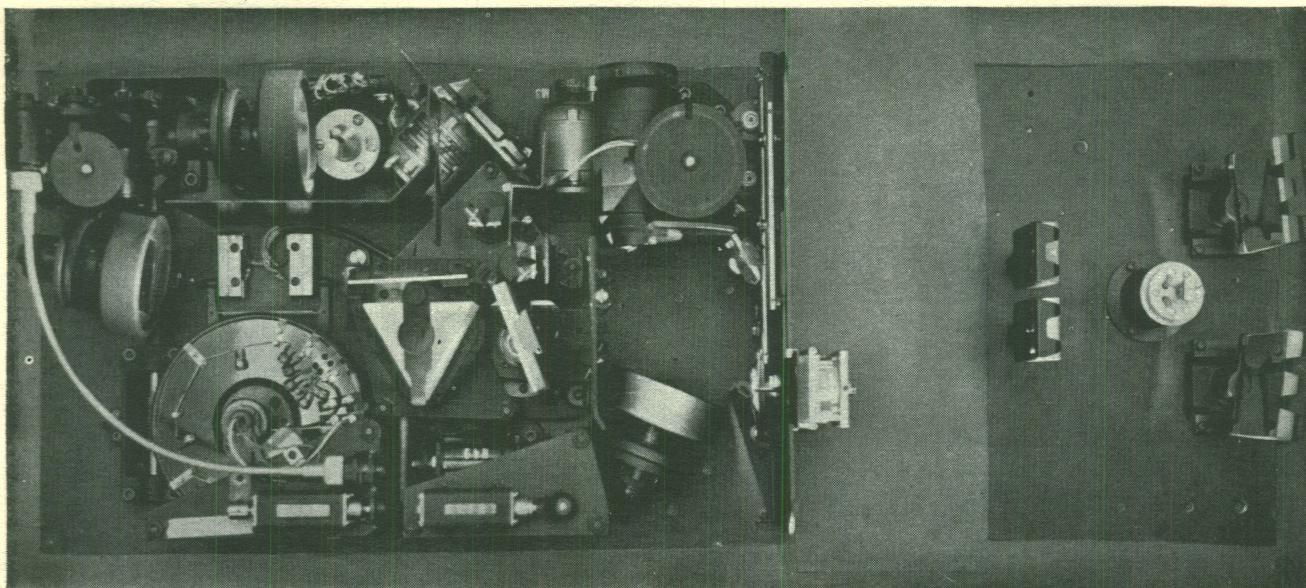
TYPES OF VIBRATION that cause most common absorption bands are here located in spectrum. Carbon atoms are represented by solid black circles, hydrogen atoms by small open circles, other atoms by squares. Carbon bonds stretch at the indicated frequencies

whether running between two carbon atoms or between carbon and a different atom. Hydrogen wagging, twisting and rocking cover the 500 to 1,300 region jointly. Plus and minus signs for wagging and twisting indicate motion in and out of plane of page.



ACRYLONITRILE, whose molecular formula appears at left, gives the infrared spectrum shown above. The curve represents the amount of energy transmitted by a sample of the mate-

rial as the wavelength increases (*from left to right*). Dips indicate frequencies at which energy is strongly absorbed, showing that a natural frequency of molecular vibration has been reached. Vibrations causing dips are indicated for comparison with chart above.



INFRARED SPECTROPHOTOMETER made by the Perkin-Elmer Corporation is shown on opposite page. Above are a photograph and diagram of its optical system. Infrared rays from a heated carbide rod (A) are split into two beams, one passing through the

sample to be analyzed (B) and the other through a wedge whose transparency can be adjusted. A rotating mirror and diaphragm (C) alternately passes the two beams, by way of a pair of mirrors, to the curved mirror (D). This reflects the beams through a prism

we just plunk the keyboard a bit, and the sounds are a bit easier to relate to the piano.

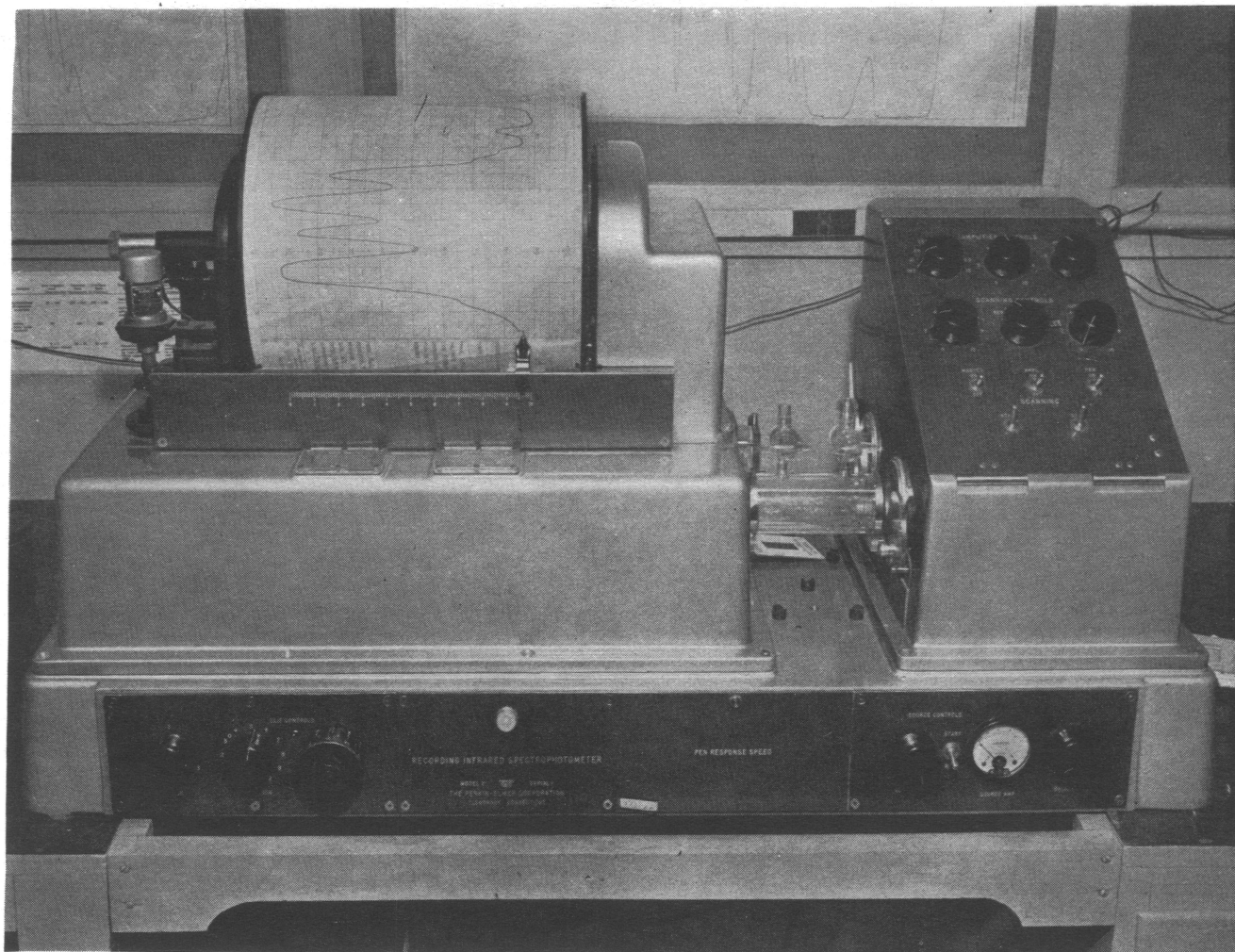
We can carry this image further. The infrared spectrum of a two-atom molecule such as HCl shows absorption not only at the single natural frequency of the bond, but also at the overtones of that frequency. A molecule containing several atoms has several bonds and several natural frequencies. Here we cannot match up the frequencies with the individual bonds. We may think of such a molecule as a mechanical system of several masses connected by springs, and the resonant frequencies will be those of such a set of coupled oscillators. When one bond is set into vibration, the rest of the molecule also is involved through the interconnecting bonds. Hence the resonant frequencies are characteristic of the *whole molecule*. They are determined by (1) the masses, which means the specific atoms involved, (2)

the spring forces, which means the bonds in the molecule, and (3) the way in which these are coupled, which means the specific geometrical arrangement of the bonds. If any of these changes, the set of resonant frequencies will change.

The infrared spectrum is simply a display of the resonant frequencies of the sample. Actually not all resonant frequencies give rise to absorption. Only those which, like the simple H-Cl vibration, cause some net change in the separation between positive and negative charges will interact with the oscillating electric field. Thus a molecule like Cl_2 , which can have no charge separation no matter how the bond length changes (one Cl is like another!), does not absorb anywhere in the infrared. One of the resonant frequencies of CO_2 , in which the two oxygen atoms move symmetrically, causes no charge displacement and hence does not appear in the infrared spectrum. But in general there

are enough active resonant frequencies in a molecule so that the infrared spectrum is characteristic of the atoms, the bonds and the geometrical arrangement.

And here we see one reason for the great value of infrared: its *specificity*. The infrared spectrum is the most nearly unique property of a substance. Even geometrical isomers, which have the same atoms and the same bonds but differ in arrangement, can be distinguished by infrared. Such isomers are very hard to distinguish by ordinary chemical methods, yet their "slight" structural differences can give rise to profound differences in biological activity. Many, perhaps most, biological phenomena are highly sensitive to such differences in compounds. Consequently medical investigators need a sensitive analytical method. The infrared spectrometer was a key tool for the late cancer researcher Konrad Dobriner at Memorial Hospital in New York City in his



which separates their wavelengths. A rocking mirror (E) sweeps the dispersed beams across the detector, by way of (D), the small plane mirror, (F), and (G). The strengths of the alternately received beams are compared at successive wavelengths. When, the

detector senses a difference between the sample and the reference beams, an alternating current is generated which adjusts the movable wedge to equalize the signals. The motion of the wedge in turn is transmitted to pen that traces the absorption curve on drum.

work of unraveling the metabolism of steroids in the body.

Inanimate objects—if internal-combustion engines can be so classified—also are sometimes sensitive to isomeric differences. The difference between “knock” and “anti-knock” gasoline components is a problem nicely suited to the infrared spectrometer. Indeed, the need in the petroleum industry for a fast, reliable and convenient method of distinguishing isomeric hydrocarbons and analyzing mixtures of them has played a large part in the recent upsurge of infrared. The war gave rise to pressing demands for high-test gasoline and for synthetic-rubber intermediates; both of these involved analysis of isomeric hydrocarbons. Infrared had been used in a few industrial laboratories in the late 1930s. Under the wartime challenge it was soon shown that infrared spectra offered the rapid and accurate analytical method so badly needed. And to meet

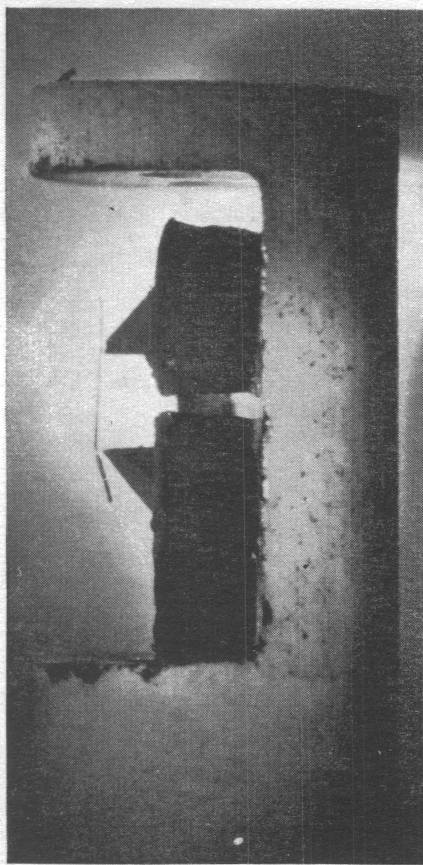
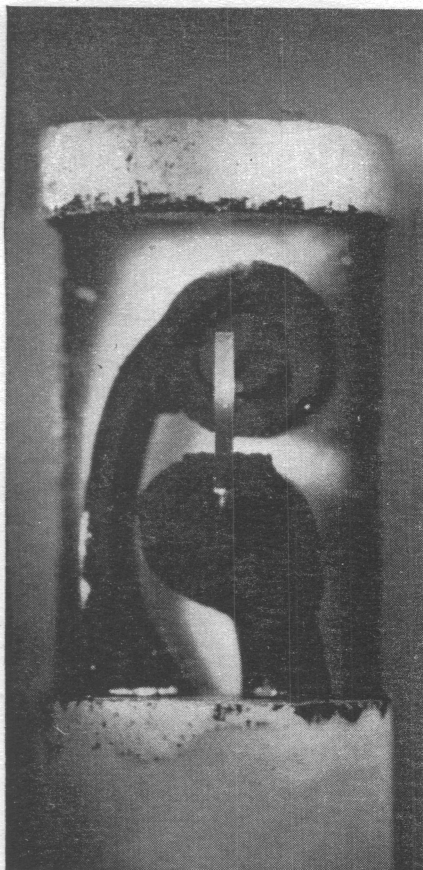
the need for instruments the first commercial infrared spectrometer appeared in 1943.

The infrared also has unusual sensitivity to atomic mass; it can distinguish not only isomers but also isotopes. Practically the only methods for analyzing the stable isotopes used in tracer work are infrared and mass spectroscopy. Which is the better method in a given case will depend on many factors; in cases calling for a fast, nondestructive analytical method applicable *in situ*, the specificity of infrared can be very useful.

Yet all this is not the whole story. The greatest advantage of infrared as a research tool is that an infrared spectrum can be interpreted in terms of the same concepts chemists use in studying chemical properties—bonds and bond groupings. In classifying compounds and thinking about them and working with them, chemists have long spoken of

“functional groups”—of olefins, of acid chlorides and so on. The functional groups provide a broad chemical description and a clue to the specific chemical properties of a compound—and they can be related to its infrared spectrum.

Let us consider for a moment the mechanical model. When two or more high-frequency springs are coupled together tightly, the vibrations of the resulting system form a new pattern in general quite distinct from that of the uncoupled springs; but when two high-frequency springs are coupled by means of a low-frequency spring, the resulting vibration pattern will include the frequencies of the high-frequency springs with only small shifts. Now chemical bonds fall approximately into two classes: (1) “high-frequency,” which includes all multiple bonds and the single bonds involving hydrogen, and (2) “low-frequency,” which includes all other single bonds, such as C-C, C-O, C-N. In



DETECTOR for spectrophotometer is shown in front view (*top*) and side view (*bottom*) about 16 times actual size. Beam of radiation is focused on thermocouple, the fine gold ribbon mounted on the contacts.

studying infrared spectra we may therefore try out the idea of a "vibrational functional group"—any set of high-frequency bonds directly connected. According to this, all molecules with the group $-N=C=S$, for example, should have some frequencies in common, but they should differ from those with the $-N=C-$ or $C=S$ groups. Here indeed we find the "something" for which Coblenz was groping!

Now we find a piece of good fortune—one of the rare presents Nature bestows on investigators. Chemical functional groups and vibrational functional groups run parallel. Therefore certain characteristic absorption bands in an infrared spectrum give direct and strong evidence on the chemical nature of the sample. It is not really conclusive evidence, for the functional group idea is an approximation, and the parallelism of chemical and vibrational functional groups is not too strict. The infrared spectrum is not a magic crystal ball in which one reads the structural formula of an unknown sample. But its clues, when wisely used, can shorten by weeks the time required to complete the job. And the direct applicability of the chemical-bond concept and the functional-group concept means that the chemist can understand infrared spectra without having to learn a new language. He *does* have to learn a new dialect of his chemical language—and incautious chemists who have overlooked this have made some serious blunders. But the dialect can be picked up relatively quickly.

The knowledge of molecular structure required to make use of infrared spectroscopy had been achieved by about 1930 or 1935. Why, then, did the blossoming of chemical infrared start only in 1943? Some pioneer applications of infrared *had* been made in the chemical industry as early as 1936. But the technique is difficult. The cost of the modern commercial instruments and their need of maintenance still remind the user that the infrared spectrometer is doing a basically harder job than its ultraviolet counterpart. It has been well said that "no other spectrometric region of the electromagnetic range is so beset with experimental difficulties." Basically these arise from the very fact that infrared radiation is resonant with atomic vibrations. We have seen the advantages stemming from this; let us glance at the price we must pay.

As a source of infrared, we must use vibrating atoms, and the only practical way to set atoms vibrating is through heat. To get a reasonable intensity of

infrared, we must heat our source to a high temperature; a common source is an electrically heated rod of carborundum at 2,200 degrees Fahrenheit. Refractory materials able to withstand such temperatures are brittle, which can be a nuisance! Moreover, the laws of physics worked out by Planck show that most of the energy goes into the near-infrared and even the visible region, wasting our power and filling our instruments with a lot of unwanted wavelengths which must be filtered out or shunted off.

The same basic trouble arises in the measurement of infrared intensity—detection, as it is appropriately called. The infrared quanta do not disturb molecules enough even to affect a photographic plate! All we can measure is a slight rise in the temperature of the absorber, and we measure it today as Herschel did—by the effect on a blackened thermometer. The "thermometer," however, is a very sensitive thermocouple.

We must find prisms to disperse the infrared spectrum and optics to focus it, windows to let the radiation through the cells holding our samples and solvents in which to dissolve materials we want to study. Since all atoms can vibrate, it is not easy to find substances transparent to the infrared. Glass and water are completely opaque to it; ordinary organic solvents have so many absorption bands themselves that they obscure the spectrum of the substance dissolved in them. So we use mirrors instead of lenses, make our prisms and cell windows of rock salt, and think hard about the choice of solvents.

For infrared, the wartime need was a blessing in disguise—a very perfect disguise, to quote Mark Twain—because urgent necessity stimulated great improvements in instrumentation. The availability of better instruments today is a great blessing not only to analytical chemists and workers in the chemical industry but also to infrared spectroscopists interested in fundamental chemistry. Infrared spectroscopy has helped us win our present understanding of molecular structure, notably the geometry and dynamics summarized in the ball-and-spring model. Nowadays more people than ever before are at work on this fundamental use of infrared, studying the nature of those springs and the distribution of electronic charges in the bonds. Without depreciating the more widespread use of infrared for the analysis of compounds, we may well feel that in the long run the fundamental use will be more exciting. For the nature of the chemical bond is the problem at the heart of all chemistry.

The Author

BRYCE CRAWFORD, JR. is chairman of the department of physical chemistry at the University of Minnesota. He was born in New Orleans in 1914 and was educated at Stanford University, where he took his Ph.D in 1937. He spent two years at Harvard University as a National Research Fellow and then taught chemistry at Yale University for a year. He has been at Minnesota since 1940. During the war Crawford did research on rocket propellants for the National Defense Research Committee and was awarded the Presidential Certificate of Merit. He has held a Guggenheim fellowship and a Fulbright grant. His research specialty is molecular structure, which he studies largely by means of

the techniques described in his article. In leisure hours he devotes himself to a scholarly interest in the treatises of Dr. Watson (but has been too busy to contribute to the *Baker Street Journal*), to model railroading and to the care and feeding of two sons.

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